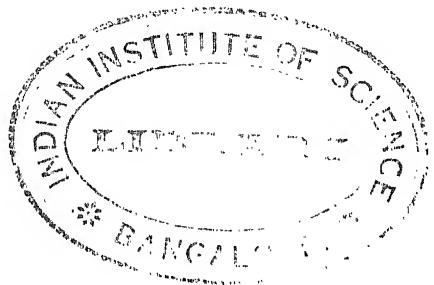
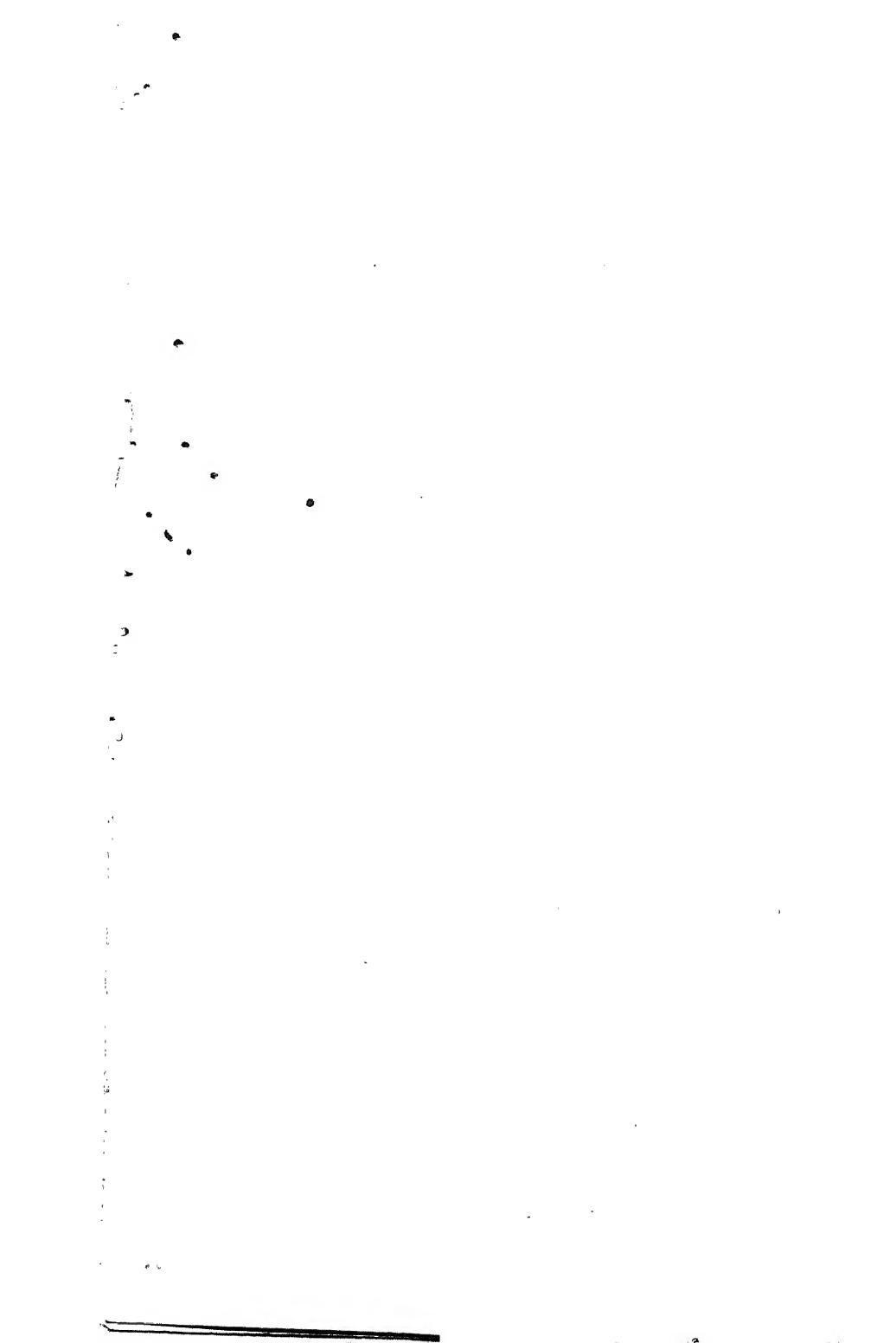


THERMODYNAMICS OF
TECHNICAL GAS-REACTIONS



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TECHNICAL GAS-REACTIONS





THERMODYNAMICS OF TECHNICAL GAS-REACTIONS

SEVEN LECTURES

BY

DR. F. HABER

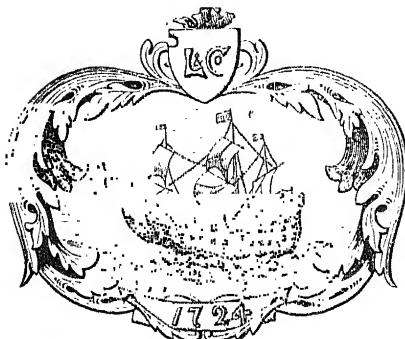
DR. PROFESSOR AT THE TECHNISCHE HOCHSCHULE, CARSRUHE

TRANSLATED BY

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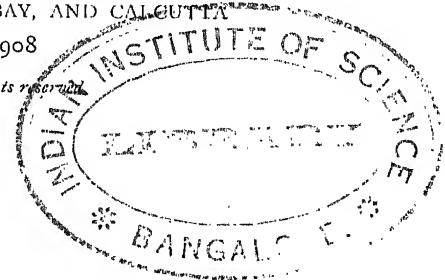
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TO
MY DEAR WIFE
CLARA HABER, PH.D.,
IN GRATITUDE FOR HER SILENT CO-OPERATION



TRANSLATOR'S PREFACE

THE fascinating possibility of predicting the course of a chemical reaction from a few characteristic constants of the reacting substances seemed very far from realization after the ill-starred attempt of Berthelot. Recent attacks upon this problem have been more successful, and the future is promising.

Prof. Haber's book entitled "Thermodynamik Technischer Gasreactionen" is a most important contribution to this subject. It is a pleasure for me to assist in making this book better known to the English-speaking world.

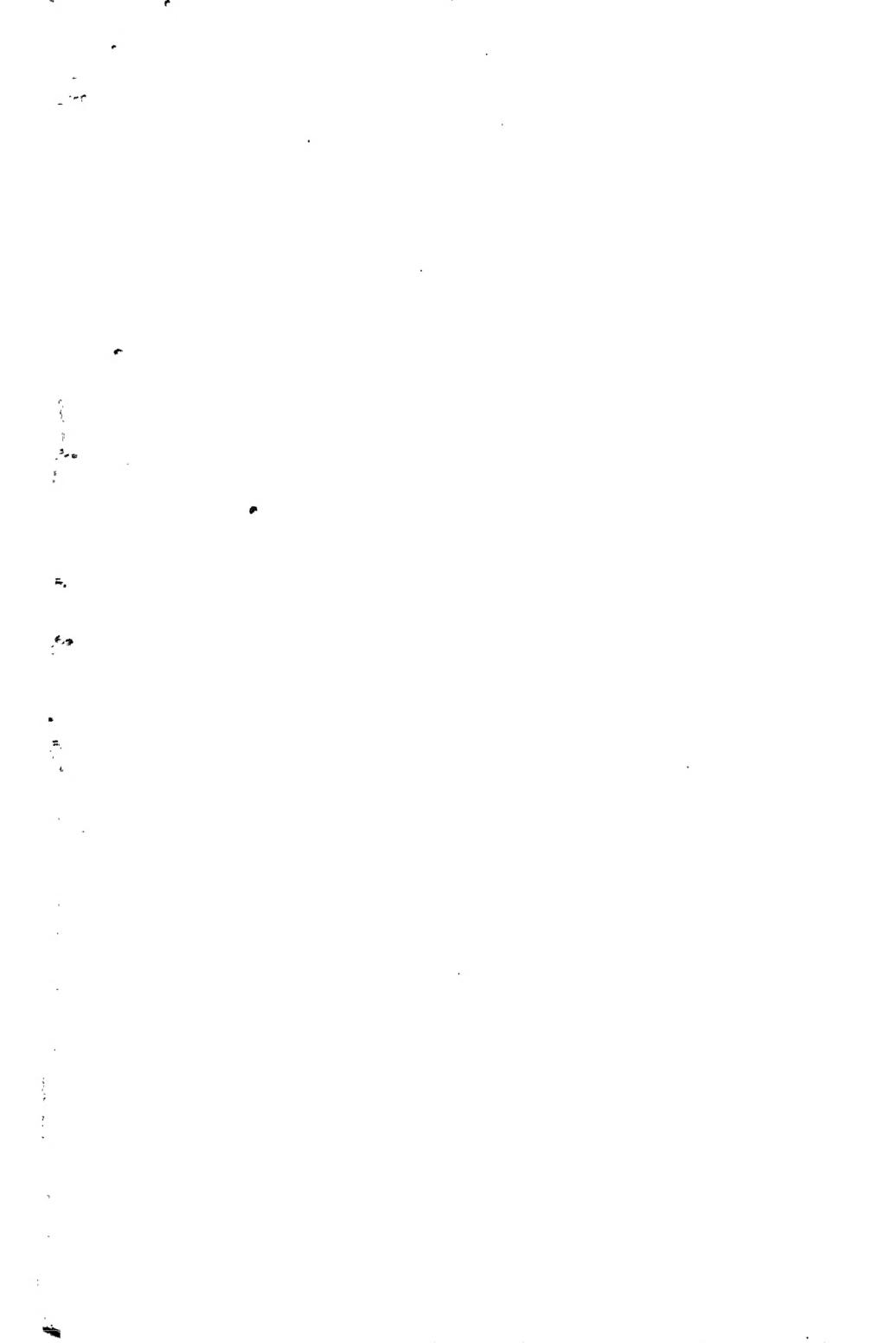
Professor Haber has thoroughly revised the German edition purposely for this translation. Many parts have been re-written, and the changes necessitated by the progress of the subject during the years 1905 and 1906 have been made. In those lectures where this involved too extensive alterations the original text has been adhered to, and the new results added in appendices. The appendix to the Third Lecture was translated by Dr. Maitland, that to the Fifth by Mr. R. Le Rossignol.

The translation of the first four Lectures was completed in its final form in the spring of 1906.

It gives me pleasure to acknowledge the valuable assistance rendered me by Dr. M. H. Hunter in the reading of the proofs.

ARTHUR B. LAMB.

NEW YORK CITY.
October 1st, 1907.



P R E F A C E

DURING February of this year I delivered a series of seven evening lectures on the thermodynamics of technical gas reactions, before several of my colleagues and a number of my younger research students. I could assume that my audience was familiar with the chemical and technical side of the subject, but was obliged to develop the mechanical theory of heat from its very foundations. These lectures, intended simply to introduce the subject for discussion by my colleagues and students, are here reproduced.

Questions asked me after the lectures, and certain difficulties which were encountered in making the subject clear, have led me to make my explanations here somewhat fuller, and to adopt the style of an essay rather than of a lecture.

I have not made use of the atomic hypothesis in these lectures. This is not due to any antagonism on my part to this hypothesis. I am simply convinced that the application of the mechanical theory of heat to chemistry becomes easier and more comprehensible the closer we restrict ourselves to the heat and work effects of masses directly perceptible to our senses.

In presenting the fundamentals of this theory, I have chosen Helmholtz's point of view. From it a chemical reaction is considered to have a latent heat just as does any simple change in the state of aggregation. Consequently, in my presentation, the two parts into which total energy can be divided are not spoken of as *free* and *bound energy*, but as *reaction energy* and *latent heat*. Various reasons have led me to adopt this less usual nomenclature. In the first place, latent heat is a concrete entity appealing directly to our senses. The idea of "bound energy" is an abstraction. Then, too, the intimate theoretical

and practical connection between gas reactions and the dissociation and vaporization of solids can be much more readily appreciated from this standpoint. Finally, starting from it, there is no difficulty in grasping both the idea of a temperature coefficient of maximum work, upon which van't Hoff, Ostwald, and Nernst based certain special considerations, and the idea of entropy which underlies Planck's method of treatment.

In connection with the work of Helmholtz, and particularly because of an article by van't Hoff in the "Festschrift" published in celebration of Boltzmann's sixtieth birthday, I have discussed at length the influence of specific heats on the energy of gaseous reactions. The *special* importance of specific heats in this kind of reactions is fully discussed at the end of the Fourth Lecture. The methods of measuring specific heats, and the data we thus far possess in this field, have also been treated at length; indeed, very much at length in some places, in order to permit the reader to criticize the choice finally made. Our knowledge of specific heats is at present so scanty that we must often trust to a sort of expert instinct in selecting proper values, without being able in some instances to prove definitely that the chosen results are really better than those of some other investigator.

The book has been written for the sake of technical rather than theoretical chemistry. I hope that it may facilitate both teaching and experimental investigation of the subject of technical gas reactions. It is not a handbook, nor does it attempt a complete presentation of all the material, but rather a clear and exhaustive treatment of the more important cases. How well I have succeeded in this clarification must be left to the decision of my colleagues.

Messrs. Gottlob and Moser have assisted me greatly in the many numerical computations contained in the book. I shall be grateful for notification of any inaccuracies of any kind which may be found.

F. HABER.

CARLSRUHE,
May 20th, 1905.

TABLE OF CONTENTS

FIRST LECTURE

THE LATENT HEAT OF CHEMICAL REACTION AND ITS RELATION TO REACTION ENERGY

	PAGE
Technical interest of gas reactions at high temperatures	2
The fundamental gas law	3
The gas constant in litre-atmospheres	4
The gas constant in absolute units	4
The calorie in absolute units	4
The gas constant in heat units	5
Equilibrium and the driving force of a reaction	5
Reaction energy and composition	6
Units of reaction energy	6
How composition may be expressed	6
Reaction energy and temperature	8
Reaction energy and reaction heat	8
The measurement of reaction heats of gases	8
Reaction heats and the decrease of the total energy	9
The determination of the reaction energy	10
The latent heat of reaction	11
Comparison with changes of state	12
The direct measurement of the latent heats	14
Latent heats and the temperature	15
The porous plug experiment	16
Isothermal gas expansion	17
Λ represents a maximum of work done	18
$\frac{d\Lambda}{dT}$ is the partial differential coefficient of Λ with respect to T	21
Integration of equation (21)	22
Peculiarities of the latent heats	23
Difference of the fundamental laws for latent heats and for the utilization of heat	24
Conditions governing the isothermal transformation of heat into work	24
The principle of Berthelot, and Helmholtz's criticism of it	25

SECOND LECTURE

ENTROPY AND ITS SIGNIFICANCE IN GAS REACTIONS

	PAGE
Reaction heat and temperature	27
Heat capacity: mean and true specific heats	28
Reaction heat at constant volume and pressure.	30
Latent heat and entropy	31
Entropy changes in non-isothermal transformations	33
Entropy changes in irreversible processes	34
The entropy of a single gas and the entropy of a gas mixture	34
Adiabatic processes	35
Non-adiabatic processes	35
Choice of the initial condition	36
Separation of gases without the expenditure of heat or work	36
The separating apparatus	37
Changes of entropy in gas reactions	38
General formulation	39
The expression of Helmholtz.	40
The thermodynamically indeterminate constant k	41
Use of Berthelot's principle to determine k	41
Other attempts at a determination of k	42
The relation of the constant k to the size of the temperature degree	43
The degree interval of the temperature scale considered for the case where $\Sigma v' = \text{zero}$	43
Influence of the size of the degree on the constant k	44
T. W. Richards' proof that k is zero in galvanic cells	45
The chemodynamic and the Celsius degree	46
Possibility of experimentally determining the value of the temperature interval	47
Alteration of the formula for $\sigma_v = f(T)$	47
Assumptions regarding the mean specific heats	48
Relation of equation (22a) to Helmholtz's more general formula	50
Again the influence of the temperature interval	51
Relation to Le Chatelier's law regarding the true specific heats	51
Use of partial pressures instead of concentrations	52
Significance of A when partial pressures are used	53
Change produced in the formula by a different definition of A	54

THIRD LECTURE

ANOTHER DERIVATION OF THE FORMULA PREVIOUSLY OBTAINED, AND ITS BEARING ON REACTIONS BETWEEN SOLIDS

Van't Hoff's diagrammatic representation	55
The roundabout way through the equilibrium box as a means of determining A	56
The maximum work is independent of the path	56

	PAGE
The <i>perpetuum mobile</i> of the second kind	56
The reaction energy deduced from van't Hoff's method of representation	58
Combination with Helmholtz's equation	59
Introduction of Kirchhoff's law	60
Substitution of partial pressures instead of concentrations	60
The thermodynamically indeterminate constant	61
Another method of combination	62
The approximation formulae	64
Van't Hoff's approximation	64
The approximation usual in theoretical physics	66
The fundamental assumption of Buff and Clausius	66
The molecular-mechanical conceptions of Clausius	67
The roughest approximation	69
When solid substances join in the reaction	69
The dissociation of calcium carbonate	70
The importance of dissociation equilibria in gas reactions	72
Other examples	73
Analogy to processes of vaporization	74
The constant of formula (28)	75
Dissociation viewed as a vaporization	75
Application of Kirchhoff's law to the phenomena of vaporization	76
The law of solid reactions	79
Dissociation and vaporization are connected quantitatively through the principle of solid reactions	80
Bearing on Trouton's rule	82

APPENDIX TO LECTURE III

Nernst's fundamental assumption	83
Nernst's own way of expressing the hypothesis	84
The thermodynamically indeterminate constants of gas reactions and of vaporization processes	86
Our notation compared with that of Nernst	88
The basis of Nernst's deduction	88
Nernst's assumption concerning the numerical values of the specific heats at the absolute zero	90
The empirical approximation of Van der Waals	94
Numerical values of the thermodynamically indeterminate constants of vaporization processes	96
Comparison of Nernst's views with those explained in the previous lectures	96

FOURTH LECTURE

EXAMPLES OF REACTIONS WHICH PROCEED WITHOUT A CHANGE IN THE NUMBER OF MOLECULES

General observations	102
Classification of the cases concerned	104

	PAGE
Case I. The formation of NO	104
Case IIa. Formation of hydrochloric acid	107
Dissociation of hydrochloric acid at higher temperatures	110
Influence of the specific heats	111
Case IIb. The formation of hydrobromic acid	112
We neglect the difference of the specific heats	114
Influence of the specific heats	114
Dissociation of hydrobromic acid at higher temperatures	115
Case IIc. The formation of hydriodic acid	115
Heat of reaction and specific heats	117
The disturbing effect of the dissociation of the iodine	119
Case III. The water-gas reaction	121
History of the water-gas reaction	122
The specific heats of the gases taking part in the water-gas equilibrium	122
Specific heat of water-vapour at low temperatures	123
Fliegnér's objections	125
Specific heat of water-vapour between 800° and 110°	126
Specific heat of CO ₂ at low temperatures	126
Specific heat of CO ₂ between 20° and 800°	127
Specific heat at high temperatures	128
How the equilibrium may be over-shot	130
Tabulation of the values for the specific heats	132
Hoitsema's consideration regarding the water-gas reaction	134
Luggin's discussion of the water-gas equilibrium	135
Experiments of Harries	138
Experiments of Bodouard	139
Experiments of Hahn	139
Hahn's results at 1205° and at 1405°	141
Velocity of adjustment of the water-gas equilibrium	141
The permeability of quartz and porcelain to gases	141
Summary	142
The thermodynamically indeterminate constant	143
Concluding remarks	145

FIFTH LECTURE

SOME EXAMPLES OF REACTIONS INVOLVING A CHANGE IN THE NUMBER OF MOLECULES

Preliminary remarks regarding numerical concentrations	147
Nitrogen dioxide and nitrogen tetroxide	149
Equilibrium constants for the formation of nitrogen tetroxide	150
Degree of dissociation of nitrogen tetroxide	150
The thermodynamically indeterminate constant for the formation of nitrogen tetroxide	151
Difference of the specific heats in the case of nitrogen tetroxide	152
Cases analogous to that of nitrogen tetroxide	153

	PAGE
Molecular compounds	154
Nitrogen dioxide	155
Nitric oxide	155
Nitrous oxide	156
Case I. The formation of carbon dioxide	156
Deville's experiment at 1300°	156
Deville's experiment with the flame	158
Le Chatelier's views regarding Deville's experiments	160
Mallard and Le Chatelier's explosion experiments	161
The relation between the explosion temperature and the explosion pressure	162
The relation between explosive pressure and degree of dissociation	162
Uncertainty of Le Chatelier's estimation	165
(1) It is not certain that equilibrium is attained	165
(2) The maximum temperatures are not strictly comparable	166
(3) The cooling action of the cold tube is difficult to allow for	166
Le Chatelier's later statements regarding specific heats	167
Observations of V. Meyer and Langer	168
Nernst's experiments	170
Le Chatelier's calculations of the dissociation of carbon dioxide	170
Comparison of Le Chatelier's results with actual observation	172
Case II. The formation of water	175
The oxy-hydrogen cell at ordinary temperatures	177
The oxy-hydrogen cell at higher temperatures	178
The Deacon chlorine process	179
The change of the catalyst during the experiment	183
Lunge and Marmier's results at 450°	186
The chemical "strength" of oxygen and chlorine	188
Case IV. The contact process for the manufacture of sulphuric acid	191
Determinations of the equilibrium constant	192
Heat of the reaction according to Bodländer and Köppen	194
Bodenstein's investigation	195
The yield	196
Clemens Winkler's contributions to the sulphur trioxide process	199
Other catalysts	200
Case IV. The formation of ammonia	202
The possible yield	204
The thermodynamically indeterminate constant	206
The inertness of nitrogen	206

SIXTH LECTURE

THE DETERMINATION OF THE SPECIFIC HEATS OF GASES

First determination of the specific heat of a gas	208
The experiments of Laplace and Lavoisier	209
Gay Lussac's experiments	209

	PAGE
Apjohn and Suermann's experiments	210
Experiment of Delaroche and Bérard	211
Experiments of Delarive and Marcket	211
Regnault's experiments	211
Regnault's accessory determinations	214
Regnault's method of experimenting with corrosive gases and with vapours	214
Wiedemann's experiments	216
The advantage of Wiedemann's modification	216
The experiments of Holborn and Austin	219
Holborn and Austin's values for carbon dioxide	220
Holborn and Henning's values for water-vapour	222
Influence of pressure on the specific heat at constant pressure	222
Joly's experiments	223
Indirect methods: explosion experiments	224
Bunsen's experiments	224
Perfecting Bunsen's method	224
Indicators	224
Measurement of impacts	225
Experiments of Berthelot and Veille, and of Mallard and Le Chatelier	225
Clerk's experiments	226
Langen's experiments	226
The crusher manometer	227
Theory of the crusher manometer	228
Experiments illustrating the theory of the crusher manometer	229
The ratio of the specific heats	231
Procedure of Clément and Desormes	232
The application of the method of Clément and Desormes	232
Cazin's experiments	233
Röntgen's experiments	233
Maneuvrier's experiments	233
Lummer and Pringsheim's experiments	234
The experiments of Müller	235
Velocity of sound in gases	236
Kundt's method	238
Capstick's experiments	239
Wüllner's experiments	239
Dust figures at high temperatures	240
Strecker's experiments	241
Acoustic method for the measurement of κ	241
Quinck's acoustic thermometer	241
Stevens' experiments	242
Kalähne's experiments	242
Low's experiments	243
Experiments of Thiesen and Steinwehr	244

SEVENTH LECTURE

THE DETERMINATION OF GASEOUS EQUILIBRIA, WITH A THEORETICAL AND
TECHNICAL DISCUSSION OF RELATED QUESTIONS

	PAGE
Physical methods for the measurement of gaseous equilibria	245
Chemical determinations of equilibria	246
Fixing the equilibrium	246
Velocity of the gaseous reaction	246
Velocity of the formation and the decomposition of hydriodic acid . .	248
Graphic representation of the influence of reaction velocity	248
False equilibria and passive resistances	249
Return to the graphic representation of the reaction velocities	251
Catalytic effects	251
Nature of catalytic action	252
Theory of reaction velocity in heterogeneous systems	252
Experience with reaction velocity in heterogeneous systems	253
Application to the combustion of coal	254
A further observation regarding the theory of heterogeneous reactions .	256
The temperature coefficient of heterogeneous reactions	256
Nernst's indirect determination of equilibria	257
Velocity of formation of nitric oxide	257
Velocity of decomposition of nitric oxide	257
Proof that equilibrium is reached	259
Reaching the equilibrium from both sides in one and the same ex- periment	259
Indirect evidence that equilibrium has been reached	261
Tests whether the equilibrium has changed during the period of cooling	261
Nernst's theory regarding the displacement of the equilibrium in a temperature gradient	263
Mathematical relation between the diffusion constant and reaction velocity, according to Nernst	263
The formation of nitric oxide in the explosion of oxy-hydrogen mixtures containing nitrogen	265
Conclusions from the results of the explosion experiments	266
Technical preparation of nitric oxide	267
The possible yield of nitric acid per unit of electricity consumed . .	267
The case of the hot arc	268
The case of the cold arc	269
Advantages of a high temperature	269
Advantages of a low temperature	269
Older attempts to prepare nitric oxide in the arc	270
Experiments of McDougall and Howles	270
The alleged mass action of the oxygen	271
The nitrogen content of the gases used in McDougall and Howles' experiments	272
Influence of the shape of the arc as found by McDougal and Howles .	273

	PAGE
Technical apparatus of Bradley and Lovejoy	273
Technical apparatus of Birkeland and Eydé	274
Theoretical discussion of the technical results	275
Return to the consideration of the explosion experiments	276
The measurement of extreme temperatures	276
Older attempts to measure temperature optically	277
Bolometric investigation of the laws of radiation	277
Fundamentals of the theory of radiation	278
Temperature radiation and luminescence	278
Solid bodies	279
Flames	279
Grey and coloured radiators	280
Small range of optically active rays	280
Kirchhoff's second principle	281
The realization of the absolutely black body	281
The experiments of Lummer and Pringsheim	281
Deduction of the law of radiation	282
Energy of radiation and the temperature	283
Maximum radiation and the displacement law of Wien	284
Bright platinum as a minimum radiator	284
Optical measurement of temperature on the basis of the laws of radiation	285
The Wien-Planck formula	285
Wanner's spectrophotometer	286
Use of the Wanner instrument	287
Measurement of total brilliancy	288
Total brilliancy and the temperature	288
Experiments of Lummer and Kurlbaum	289
Example of the application of the optical method of measuring temper- ature	291
Special applicability of the optical method to determinations of equilibria	291
Measurements upon luminous flames	292
Uncertainties in measuring the temperature of luminous flames	294
Measurement of non-luminous flames	295
Thermoelectric measurement of the temperature of flames	296
Conditions necessary for the accurate thermo-electric measurements of the temperature of flames	297
Effect of the duration of the heating in the flame	298
Effect of internal resistance	298
Effect of the position of the wires	299
The Bunsen flame	299
Steadying the Bunsen flame	300
The interior of the flame	300
The location of the inner cone	300
The location of the outer cone	301
The temperature of the inner cone	301
Heat losses of the inner cone	302
Temperature distribution between the cones	302

	PAGE
Splitting the Bunsen flame	303
Analysis of the sample of gas	305
The calculation of the analysis	306
Discussion of Wohl's formula	306
Justification of Bunsen's formula	307
The water-gas equilibrium in the Bunsen flame	308
The limits within which equilibrium can be attained and maintained in the Bunsen flame	309
Numerical results	309
A theoretical discussion of the technical process of water-gas manufacture	310
The usual conception	310
Boudonard's experiment	311
The peculiar action of coal	312
Survey of the matter from a technical standpoint	312

APPENDIX TO LECTURE V

The experiment of Nernst and v. Wartenberg on the dissociation of CO_2	315
Langmuir's experiments	317
The glass cell	318
Theory of the glass cell	318
Comparison with the chlorine cell	319
Results with the glass cell	319
Löwenstein's density experiments	321
Emich's dust experiments	321
Emich's determination of the duration of outflow	322
Summary of the results on the dissociation of CO_2	322
Comparison of the old and the new figures	323
Dissociation of H_2O	324
Glass and porcelain cells	324
Influence of water vapour discussed theoretically	324
The free energy of the formation of water from the elements	325
Values found with glass and porcelain cells	328
Patterson's work on the oxy-hydrogen cell	329
Lewis's work on the oxy-hydrogen cell	329
Nernst and v. Wartenberg's experiments on the dissociation of water-vapour	330
Experiments of Löwenstein on the dissociation of water-vapour	331
Experiments of Langmuir and Holt	332
Summary of the data on the dissociation of water-vapour	332
The Deacon process	333
Lewis' experiments	333
Vogel v. Falkenstein's experiments	335
Results and calculations	336
Experiments of Levi and Battioni	337
APPENDICES TO LECTURE VII	338
INDEX—Subjects	347
Names	353

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THERMODYNAMICS

FIRST LECTURE

THE LATENT HEAT OF CHEMICAL REACTION AND ITS RELATION TO REACTION ENERGY

GENTLEMEN,—In these lectures I shall endeavour to make clear the significance of heat factors in gas reactions, with especial reference to the specific heats of the interacting substances and to the heat evolved during the reaction.

Thermochemistry concerns itself in general with the total amount of heat evolved (or absorbed) during the whole course of a reaction, but leaves quite untouched the question as to whether the reaction goes to completion in one direction or halts in an intermediate (equilibrium) condition.

All simple gas reactions do halt at such equilibrium conditions, and are consequently incomplete. Often, indeed as a rule, this incompleteness only becomes perceptible at high temperatures.¹ But phenomena at high temperatures are precisely what interest us here. In the region of low temperatures, gases often react very sluggishly with one another. The reaction velocities are then the governing factors of the process, and these are not to be predicted in advance from the standpoint of the theory of heat. The higher the temperature rises the less important do these factors become, while the equilibrium phenomena which are subject to theoretical treatment attain prominence. These equilibrium phenomena² are all that we shall concern ourselves with here.

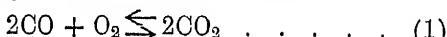
¹ Theoretically every reaction belongs to this class, and may therefore be termed reversible. But it must be possible to demonstrate experimentally his reversibility under any conditions if its theoretical consideration is to be scientifically useful.

² Here we mean only "real" equilibria, which can be reached from both sides. The "false" equilibria, which can be reached from one side only, and their relation to passive resistance and reaction velocity, will be discussed in the last lecture.

They have often been discussed in relation to the mass action of the reacting substances, but the influence exerted by the specific heat of the substances has received but little attention. Le Chatelier,¹ to be sure, showed long ago, in a comprehensive work on dissociation, the importance of specific heats, but this work was not accorded the general notice which it deserved. The result is that our knowledge of the subject is limited and the number of cases at our disposal is scanty. The subject has, however, so broad a significance that it is well worth our while to become conversant with it. Only when we consider the joint effect of mass action and the specific heats of the reacting substances are we able, from observations made at any one temperature, to draw inferences regarding the phenomena which will take place at a temperature, say a thousand degrees higher. The theory even affords us the expectation of being able to find out all about a gas equilibrium at high temperatures, simply from a knowledge of the heat factors concerned, without any experimental determinations of mass actions.² Satisfactory confirmation, however, of this last step is lacking, because our knowledge of the specific heats of gases is as yet too incomplete.

Technical
interest
of gas
reactions
at high
tempera-
tures.

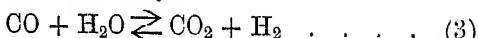
Gas reactions at high temperatures frequently possess a very great practical interest. We should mention, in the first place, those heating processes where carbon dioxide and water vapour are formed. These substances dissociate at very high temperatures into free oxygen, carbon monoxide, and hydrogen. The effect of temperature and the composition of the gas mixture on the dissociation of the carbon dioxide and the water-vapour is a first question of importance, which must be solved by means of the mechanical theory of heat. The two reactions—



and



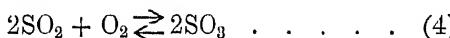
are connected with one another by the relation—



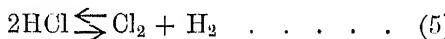
¹ *Annales des Mines*, viii. 13 (1888), 157.

² Since the publication of the German edition of this book, Nernst has given his views on this problem. See his "Thermodynamics and Chemistry" (Chas. Scribner's Sons, New York, 1907). An account of them will be found at the end of the Third Lecture.

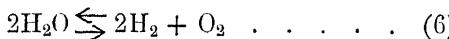
We can decide in which direction this so-called "water-gas reaction" will proceed at a given concentration of the four substances in the gas mixture, and at a known high temperature, when the dissociation conditions represented in (1) and (2) are known. Dissociation of this kind also possesses a great significance in technical inorganic chemistry. The reaction—



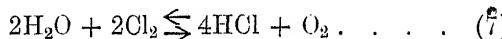
forms, as is well known, the foundation of the modern method of sulphuric acid manufacture. The two reactions—



and



taken together, give us Deacon's chlorine process—



The possibility of making ammonia from its elements, and nitric oxide, and consequently nitric acid and the nitrates, from the air, is governed by the relationships given by the mechanical theory of heat for the reactions—



and



The fundamental thermodynamic relations which we will consider can be applied to the reactions of solids, liquids, and gases. They are employed under the most varied forms, ^{fundamental} gas law. especially for molten and dissolved substances. But they assume a particularly simple form for gaseous substances, because in these the pressure, temperature, and volume are connected by a very simple relation, while in the case of molten or dissolved substances no similar general relation connecting these three quantities is known. This relation is—

$$pv = RT \dots \dots \dots \quad (10)$$

where p = pressure and v = volume. If we consider a mol as the unit of mass, experiment shows us that at a pressure of one atmosphere (*i.e.* at 760 mm. Hg at sea-level and latitude 45°) this unit of mass occupies 22.412 litres at a temperature of 0°. Equation (10) requires that the temperature be reckoned in

degrees on the absolute scale. The zero point of this scale is generally put at -273°C . It is equal to minus the reciprocal value of the coefficient of expansion of an ideal gas (273). The coefficients of ordinary gases are very slightly different from this. By careful consideration of the deviation from the behaviour of ideal gases which ordinary gases show on compression and expansion it is possible to find the coefficient of expansion of ideal gases.¹ It amounts to $\frac{1}{273.09}$. The absolute zero therefore is, strictly speaking, not at -273°C , but 0.09° lower.²

This difference will be too small to be considered in our later calculations, but we must take account of it here, in order to determine R with all possible precision. We then got—

The gas constant in litre-atmospheres.

$$e = \frac{22.412 \times 1}{273.09} = 0.08207$$

This value of R is expressed in litre \times atmosphere units (litre-atmospheres). If we compute the volume in cubic centimetres and the pressure in dynes per square centimetres, it becomes—

The gas constant in absolute units.

$$R = \frac{22.412 \times 76 \times 13.596 \times 980.6}{273.09} = 0.83155 \times 10^8 \text{ abs. units } \left(\frac{\text{erg}}{\text{sq. cm.}} \right) T$$

Here 76 is the height in centimetres of a column of mercury which exerts a pressure of one atmosphere; 13.596 the weight in grams of a cubic centimetre Hg; and therefore 76×13.596 the weight of the mercury column which exerts a pressure of one atmosphere per square centimetre. Since the gram weight at sea-level and lat. 45° corresponds to 980.6 dynes, then $76 \times 13.596 \times 980.6$ is the pressure in absolute measure of an atmosphere on a unit of surface (1 sq. cm.); that is, the pressure on a piston 1 sq. cm. in area working in a cylinder containing 1 mol (22,412 c.c.) of gas.

For our purposes it is most convenient to measure R in heat units (gram calories). We therefore need to know the value of a gram calorie in absolute units.

¹ For the theory see Mach, "Prinzipien der Wärmelehre" (1900), 2nd edit., p. 309 (or translation).

² Daniel Berthelot, *Z. f. Electrochemie*, x. (1904), 621; and Nernst, *idem.*, 629.

This value depends upon the temperature at which it is determined. At present it is usual to define a calorie as that quantity of heat which will warm 1 gram water from 15° to 16° .¹ The quantity of heat required to raise 1 gram of water from 0° to 1° is greater than this by 0·06 per cent. This somewhat larger zero-point calorie used to be (till about 1880) preferred. In its stead Schuller and Wartha² substituted the quantity of heat necessary to heat 0·01 gram of water from 0° to 100° . (Ostwald³ took a hundred times this value as a unit and called it K.) This "mean calorie" is very nearly equal to the 15° calorie.⁴ The mechanical equivalent of heat has been set by the Committee on Units of the Deutschen Bunsengesellschaft as equal to $41\cdot89 \times 10^6$ erg.⁵

We get from this—

$$R = \frac{0\cdot83155 \times 10^8}{41\cdot89 \times 10^6} = 1\cdot98507 \left(\frac{\text{grain-cal.}}{T} \right)$$

The gas constant in heat units.

We shall use later, in our numerical calculations, the abbreviated value 1·98, which is very near the exact value of R computed on the basis of the 15° calorie, the zero-point calorie, and the mean calorie.

The reactions (1) to (9) all proceed till they reach an equilibrium. Indeed, the characteristic of the equilibrium condition is that there the reaction will not of itself spontaneously progress in either the one or the other direction. That is, the driving force of a chemical reaction is zero at the equilibrium point. If we know the composition of the gas mixture at equilibrium for any given temperature, then for any other composition of the gas mixture at the same temperature the driving force of the reaction is given by the *distance from the equilibrium point*.

We should at first be inclined to call the reaction energy

¹ Or more accurately from $15\frac{1}{2}^{\circ}$ to $16\frac{1}{2}^{\circ}$. Compare Warburg's report on the unit of heat read before the Naturforscherversammlung in Munich (1899, "Bericht über die Verhandlungen," p. 62).

² *Wied. Ann.*, 2 (1877), 365.

³ *Lehrb. d. allg. Chemie*, II₂ (Leipzig, 1893), p. 72.

⁴ According to Belm (Drude's *Ann.*, 16 (1905), 653), the mean calorie is greater by 0·03 per cent., according to Dieterici (*idem.*, p. 593), 0·2 per cent. greater, than the 15° calorie. Other figures are given by Planck ("Thermodynamik" (Leipzig, 1905), 2nd edit., p. 31).

⁵ *Zeitschr. f. Elektrochemie*, ix. (1903) 686.

the total work which a chemical reaction can do during its whole course. This definition, however, is unsuitable for theoretical treatment.

Reaction energy and composition. The driving force of a chemical reaction changes continuously with the changing composition of the reacting mixture. The nearer we approach the equilibrium point where the reaction stops, the smaller does this driving force become. We take as units of transformation, the transformation of such amounts as appear in equations (1) to (9). Thus, in reaction (2), the change of one mol O_2 , two mols H_2 , into two mols H_2O is the unit of transformation. The reaction energy of every infinitely small fraction dx of this unit quantity is equal to the driving force A multiplied by the quantity transformed, that is $A \times dx$. To get the total energy of transformation, we must find the sum of all the quantities $A \times dx$ with the aid of the integral calculus, having first expressed A as a function of x . Such an expression would be awkward and involved. It is therefore better to consider the quantity of gas so great that the transformation of a unit quantity would have no appreciable effect on the composition of the mixture, and consequently cause no appreciable change in its driving force. We then get for the product of the driving force into the unit quantity transformed (that is, one mol) the value $A \times 1 = A$, and consider this as the reaction energy. The value A of the reaction energy, therefore, characterizes only a single tiny phase in the progress of the reaction, during which the composition remains constant. It shows us, however, how far we are from the end of the reaction or the equilibrium point where $A = \text{zero}$, and this is the important thing.

Measure of reaction energy. The reaction energy A may be expressed in any units of energy which suit our convenience. In what follows, we shall always measure it in gram calories, taking for practical reasons as far as possible the 15° calorie as our unit of heat. However, the older data are often expressed without any precise definition of the calorie used, and the possibility even of a sure recalculation is not always afforded by the data given. The smallness of the difference between the mean, the zero and the 15° calorie makes this uncertainty less troublesome.

How composition. Considering the composition of the gas as invariable during the reaction, we are at liberty to express this composition either